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(54) **Flame retardant polyamide polyphenylene ether compositions**

(57) The invention is directed to a polymer composition comprising:

- a) a blend comprising at least one polyamide and at least one polyphenylene ether;
- b) at least one polymeric siloxane compound; and
- c) at least one boron compound.

EP 0 714 951 A1

Description

This invention relates to novel polyamide-polyphenylene ether compositions

Polymer blends which contain polyamide and polyphenylene ethers (PPE) constitute an invaluable class of engineering thermoplastic resins. Resins of polyphenylene ethers are characterized by a unique combination of chemical, physical and electrical properties. For instance, they are resistant to many solvents and generally display high impact strengths. As a result of this unique combination of properties, resins of polyphenylene ethers are suitable for a broad range of commercial applications.

Efforts have been made to prepare polymer blends which, while retaining their characteristic hydrolytic stability, dimensional stability and dielectric properties, have higher heat deflection temperatures. Particularly, there is a demand for immiscible blends, like polyamide blends, which possess increased heat deflection properties since they are, for instance, conventionally used in parts exposed to high temperatures in the automotive industry.

While thermoplastic resins and blends possess the above-described advantageous properties, they, like many other organic polymeric materials, are particularly desired when they possess flame retardant properties.

It is of increasing interest to prepare thermoplastic resins and blends prepared therefrom that are fire resistant. Such preparation conventionally employs adding flame retardant additives to the polymer/blend. However, blends comprising said flame retardant additives are invariably environmentally unfriendly.

In addition thereto, the inclusion of fire retardant additives usually influences the mechanical properties (impact resistance; heat resistance) negatively.

The instant invention, therefore, is directed to novel polymer compositions that display superior flame retardant properties.

Efforts have been made to prepare polyamide-PPE compositions that possess flame retardant properties. In U.S. Patent 4,866,144, self-extinguishing thermoplastic polyphenylene ether/polyamide molding materials are disclosed. Said materials comprise triazine compounds such as cyanuric acid, cyanuric acid derivatives and mixtures thereof and preferably melamine and/or melamine cyanurate as flame proofing agents.

Other investigators have focused their attention on polyamide blends in order to improve flame retardancy. European Patents 0436136 and 0129825 describe blends of polyphenylene ethers and polyamides comprising phosphorus containing compounds in order to enhance flame retardant properties.

Still others, such as those described in European Patent 0369169, have revealed polymer compositions comprising polysiloxanes, polyamides and polyphenylene ethers having flame retardant properties.

The instant invention is based on the observations that polyamide-PPE compositions comprising boron compounds and polysiloxane compounds unexpectedly display flame retardant properties and good heat resistances. Moreover, the instant polyamide-PPE compositions do not contain halogens and red phosphorus.

Accordingly the invention is directed to novel polyamide-PPE compositions that unexpectedly display flame retardant properties and improved heat resistances, said composition comprising:

- a) a blend comprising at least one polyamide and at least one polyphenylene ether;
- b) at least one polymeric siloxane compound; and
- c) at least one boron compound

In the instant invention, flame retardant properties mean that UL-94 is V-O or V-1 at 1.6 mm and improved heat resistance mean a Vicat of greater than about 200°C, wherein the Vicat temperature is the softening temperature at which a plastic starts to soften as specified according to ISO 306.

The present invention is based on the surprising discovery, that the use of a polymeric siloxane compound, preferably polysiloxane, in combination with boron compounds provides an improved flame retardant action in polyamide-polyphenylene ether blends. More in particular it is important that the negative influence of those compounds on the mechanical properties, such as impact resistance (IZOD) and heat resistance (Vicat) is relatively low, especially in comparison to the other environmentally friendly flame retardant additives.

According to the present invention the polymer composition comprises as main components the PA-PPE blend, polysiloxane, at least one boron compound, and as optional components inorganic phosphate and titanium oxide. The use of organic based phosphorous compounds (such as organic phosphate and phosphine oxides) is not precluded in relation to the present invention, however, in view of their negative influence on the Vicat temperature they are not recommended.

The polyphenylene ethers employed in the instant invention are typically prepared by the oxidative coupling of at least one monohydroxyaromatic compound such as 2,6-xylenol or 2,3,6-trimethylphenol. Catalyst systems are generally employed for such coupling; they typically contain at least one heavy metal compound such as a copper, manganese or cobalt compound, usually in combination with various other materials.

Furthermore, polyphenylene ethers suitable for use in the practice of the present invention may be prepared by any of a number of processes utilizing precursor corresponding phenols or derivatives thereof. Examples for their production

are disclosed in U.S. Patents 3,306,874; 3,306,875; 3,257,357; 3,257,358; 3,337,501; and 3,787,361, all incorporated herein by reference

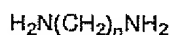
Additional useful polyphenylene ethers are those which comprise molecules having at least one aminoalkyl-containing end group. The aminoalkyl radical is typically located in an ortho position to the hydroxygroup. Products containing such end groups may be obtained by incorporating an appropriate primary or secondary monoamine such as di-n-butylamine or dimethylamine as one of the constituents of the oxidative coupling reaction mixture. Also frequently present are 4-hydroxybiphenyl end groups, typically obtained from reaction mixtures in which a by-product diphenoquinone is present, especially in a copper-halide-secondary or tertiary amine system. A proportion of the polymer molecules may contain at least one of said aminoalkyl-containing and 4-hydroxybiphenyl end groups

The polyamides employed in the instant invention are obtained, for instance, by polymerizing a monoamine-mono-carboxylic acid; or a lactam thereof having at least 2 carbon atoms between the amino and carboxylic acid group or by polymerizing substantially equimolar proportions of a diamine which contains at least 2 carbon atom amino groups and a dicarboxylic acid; or by polymerizing a monoaminocarboxylic acid or a lactam thereof as defined hereinabove together with substantially equimolar proportions of a diamine and a dicarboxylic acid. The dicarboxylic acid in the form of a functional derivative thereof; for example, an ester or acid chloride.

The term "substantially equimolecular" proportions (of the diamine and of the dicarboxylic acid) is used to cover both strict equimolecular proportions and slight departures therefrom which are involved in conventional techniques for stabilizing the viscosity of the resultant polyamides

Examples of the aforementioned monoaminomonocarboxylic acids or lactams thereof which are useful in preparing the polyamides include those compounds containing from 2 to 16 carbon atoms between the amino and carboxylic acid groups, said carbon atoms forming a ring with the -CO-NH-group in the case of a lactam. As particular examples of aminocarboxylic acids and lactams there may be mentioned aminocaproic acid, butyrolactam, pivalolactam, caprolactam, capryl-lactam, enantholactam, undecanolactam, dodecanolactam and 3- and 4-aminobenzoic acids

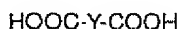
Diamines suitable for use in the preparation of the polyamides include straight chain and branched, alkyl, aryl and alkyl-aryl diamines. Such diamines include, for example, those represented by the general formula I



I

wherein n is an integer of from 2 to 16, such as trimethylene diamine, tetramethylene diamine, pentamethylene diamine, octamethylene diamine and especially hexamethylene diamine, as well as trimethyl hexamethylene diamine, meta-phenylene diamine, meta-xylene diamine and the like.

The dicarboxylic acids may be aromatic, for example, isophthalic and terephthalic acids. Preferred dicarboxylic acids are of the formula II



II

wherein Y represents a divalent aliphatic group containing at least 2 carbon atoms, and examples of such acids are sebacic acid, octadecanedioic acid, suberic acid, glutaric acid, pimelic acid and adipic acid

Typical examples of polyamides (Nylons) useful in the instant polyamide compositions include for example polyamides 4/6, 6, 6/6, 11, 12, 6/3, 6/4, 6/10 and 6, 12 as well as polyamides resulting from terephthalic acid and/or isophthalic acid and trimethyl hexamethylene diamine, polyamides resulting from adipic acid and meta xylylene diamines, polyamides resulting from adipic acid, azelaic acid and 2,2-bis-p-aminocyclohexyl)propane, semi-crystalline polyamides resulting from combinations of terephthalic and/or isophthalic and/or adipic acids with hexamethylene diamine, semi-crystalline polyamides resulting from terephthalic and/or isophthalic acids and hexamethylene and 2-methyl pentamethylene diamines, and polyamides resulting from terephthalic acid and 4,4'-diamino-dicyclohexylmethane. Mixtures and/or copolymers of two or more of the foregoing polyamides or prepolymers, respectively, are also within the scope of the present invention. Preferred polyamides are the polyamides 6, 6/6, 6/10 and 4/6, most preferably polyamide 6/6.

It is also understood that use of the term "polyamides" herein and in the appended claims is intended to include the toughened or super tough polyamides. Super tough polyamides or super tough nylons, as they are more commonly known, are available commercially, e.g., from E. I. duPont under the tradename Zytel ST, or may be prepared in accordance with a number of U.S. patents, including, among others, Epstein, U.S. Patent 4,174,358; Novak U.S. Patent 4,474,927; Roura, U.S. Patent 4,346,194; and Joffrion, U.S. Patent 4,251,644, herein incorporated by reference. These super tough nylons are prepared by blending one or more polyamides with one or more polymeric or copolymeric elastomeric toughening agents. Suitable toughening agents are disclosed in the above-identified U.S. patents, as well as in Caywood, Jr., U.S. Patent 3,884,882 and Swiger, U.S. Patent 4,147,740 and Gallucci et al., "Preparation and Reactions of Epoxy-Modified Polyethylene", J Appl. Poly., Sci., Vol. 27, pp. 425-437 (1982) herein incorporated by reference. Typically, these elastomeric polymers and copolymers may be straight chain or branched as well as graft polymers and copolymers, including core-shell graft copolymers, and are characterized as having incorporated therein either by copo-

lymerization or by grafting on the performed polymer, a monomer having functional and/or active or highly polar groupings capable of interacting with or adhering to the polyamide matrix so as to enhance the toughness of the polyamide polymer.

While it is preferred that the polyamide compositions of the instant invention comprise blend of polyamides and polyphenylene ethers, it is also within the scope of this invention to include in said compositions acrylic polymers including polymethylmethacrylate, acrylonitrile styrene copolymers, styrene-acrylonitrile-butadiene copolymers, polyvinyl chloride, polystyrene, butyrates, polyaliphatics, polycarbonates and polyesters, cellulosic, phenolic, amino and epoxy resins.

It is also within the scope of the instant invention to employ compatibilization agents in the blends. Such compatibilization agents include, for instance, compounds selected from the group consisting of tetracarboxylic acids of aromatic and aliphatic compounds, alicyclic compounds, dianhydride derivatives and halogen substituted phthalic anhydrides. A more detailed description of blend compatibilization may be found in U.S. Patent 4,826,933, the disclosure of which is incorporated herein by reference.

The blending ratio of polyamide to polyphenylene ether units is about 5 to about 95% by weight, preferably about 10 to about 70% by weight of polyphenylene ether to about 90 to about 30% by weight of polyamide.

Impact modifiers for polyphenylene ether-polyamide blends are well known in the art. They are typically derived from one or more monomers selected from the group consisting of olefins, vinyl aromatic monomers, acrylic and alky-lacrylic acids and their ester derivatives as well as conjugated dienes. Especially preferred impact modifiers are the rubbery high-molecular weight materials including natural and synthetic polymeric materials showing elasticity at room temperature. They include both homopolymers and copolymers, including random, block, radial block, graft and core-shell copolymers as well as combinations thereof.

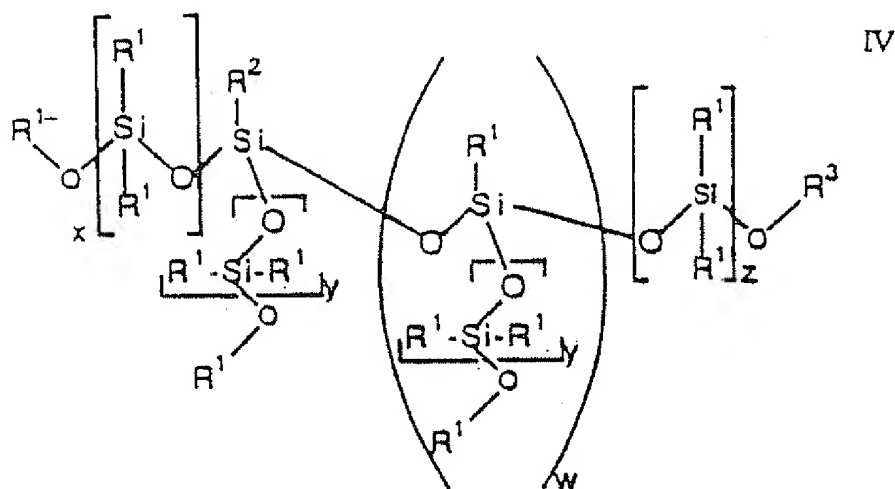
A particularly useful class of impact modifiers comprises the AB(diblock) and ABA (triblock) copolymers and core-shell graft copolymers of alkenylaromatic and diene compounds, especially those comprising styrene and butadiene or isoprene blocks. The conjugated diene blocks may be partially or entirely hydrogenated, whereupon they may be represented as ethylene-propylene blocks or the like and have properties similar to those of olefin block copolymers. Examples of triblock copolymers of this type are polystyrene-polybutadiene-polystyrene (SBS), hydrogenated polystyrene-polybutadiene-polystyrene (SEBS), polystyrene-polyisoprene-polystyrene (SIS), poly(α -methylstyrene)-polybutadiene-poly(α -methylstyrene) and poly(α -methylstyrene)-polyisoprene-poly(α -methylstyrene). Particularly preferred triblock copolymers are available commercially as CARIFLEX®, KRATON D® and KRATON G® from Shell.

Also suitable as impact modifiers are the ionomer resins, which may be wholly or partially neutralized with metal ions, and the core-shell type graft copolymers. In general, the latter have a predominantly conjugated diene or crosslinked acrylate rubbery core and one or more shells polymerized thereon and derived from monoalkenylaromatic and/or acrylic monomers alone or in combination with other vinyl monomers. Included are copolymers wherein an interpenetrating network of the resins employed characterizes the interface between the core and shell, such as those available from General Electric Company and described in U.S. Patent 3,944,631.

Other impact modifiers include the above-described types containing units having polar groups or active functional groups, as well as miscellaneous polymers such as Thiokol rubber, polysulfide rubber, polyurethane rubber, polyether rubber (e.g., polypropylene oxide), epichlorohydrin rubber, ethylene-propylene rubber, thermoplastic polyester elastomers and thermoplastic ether-ester elastomers.

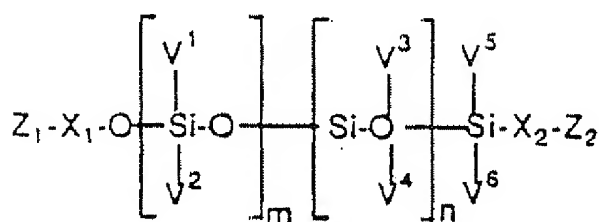
Additionally, the polyamide and polyphenylene ether blends may further comprise, for instance, functionalized polyphenylene ethers, polycarboxylic acids, ester groups, epoxy groups, anhydride groups, rubbers or any other conventional moiety employed to improve the properties of the blend.

The polymeric siloxane compound used in the present invention may be selected from the group of polysiloxane and siloxane copolymers, such as polyphenylene ether or polyetherimide siloxane copolymers. The preferred polysiloxane compounds employed in the instant invention are commercially available and are represented by the formula IV

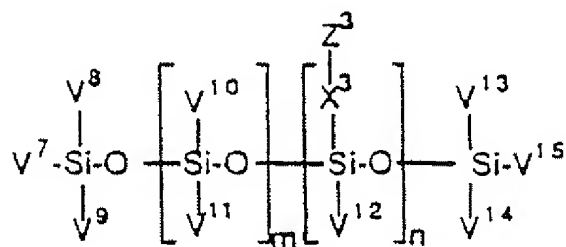


wherein each R^1 is independently a C_{1-5} alkyl group and preferably a methyl group and R^2 is a C_{1-5} alkyl group or a primary or secondary amino group such as a N-(2-aminoalkyl)-3-aminoalkyl group, provided that R^2 is a C_{1-5} alkyl group when w is 1 and a N-(2-aminoalkyl)-3-aminoalkyl group when w is 0. It is often preferred that R^2 is a methyl group or a N-(2-aminoethyl)-3-aminopropyl group. R^3 is hydrogen or a C_{1-5} alkyl group, preferably a methyl group. w is 0 or 1 and x and y are each independently an integer from 1 to 7 and z is an integer from 0 to 7. It is noted herein that any combination of compounds represented by formula IV may be employed

It is also within the scope of the invention to employ polysiloxanes represented by the formulae V and VI



and



wherein $m + n$ has a value of 5-2000, $V1-V15$, each independently of each other, represent a hydrogen atom or one of the following groups having 1-12 carbon atoms: alkyl, alkoxy, alkenyl, aryl, aralkyl, alkylaryl, which groups may be halogenated; wherein X_1, X_2, X_3 , each independently of each other, represent one of the following groups; alkylene, cycloalkylene, arylene, aralkylene, alkylarylene; wherein Z_1, Z_2, Z_3 each represent one of the following groups: -
 5 $NV16V17-NH-(CH_2)_q-NV16V17$ in which $V16$ and $V17$, each independently of each other, represent a hydrogen atom or an alkyl group having 1-12 carbon atoms. q has a value from 1-10, an aliphatic or cycloaliphatic epoxide, a carboxylic acid or anhydride group, Z_1 or Z_2 is a hydrogen atom, in which, however, the compound of formula V may not comprise simultaneously an amine group and an epoxide group or not simultaneously an amino group and a carboxylic acid group, or not simultaneously an epoxide group and a carboxylic acid or anhydride group.

10 One of the important components of the present invention is the boron compound. Within the scope of the present invention organic and inorganic boron compounds may be used, the amount of the compounds being such that the boron content of the polymer composition, calculated as atomic boron, is between 0.02 and 5, preferably between 0.2 and 1 wt.%.
 Suitable boron compounds are i.a. boric acid, metal borates, boron phosphate, perborates and the like. More in particular preferred are metal borates (and perborates), such as alkali metal borate (sodium, potassium etc), alkaline earth borates (calcium, barium and magnesium) and transition metal borates, such as zinc borate. Those metal borates, but also the metal perborates, are preferably used in the anhydrous form.

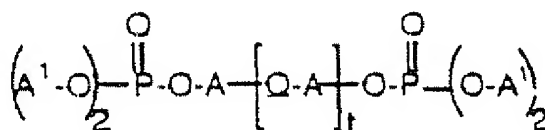
15 According to the invention the composition additionally may contain inorganic phosphates and/or titanium oxide. Examples of suitable inorganic phosphates are the alkali metal (including ammonium) phosphates, alkali metal hydrogen phosphates, alkali metal pyrophosphates and the like. In a specifically preferred embodiment the boron compound and the inorganic phosphate may be combined in boron phosphate, which gives a clearly improved flame retardant action. Also the use of titanium oxide improves the properties of the polymer composition.

20 As the use of calcium sulphate has been found to improve the comparative tracking index, the use thereof in the compositions of the invention, preferably in amounts between 5 and 20 wt. % of the composition is preferred. The amounts of both the phosphate compound and the titanium oxide may be selected within wide ranges, each being preferably between 0.1 and 20 wt. % of the total of the polymer composition.

25 It is also noted herein that the polyamide compositions of this invention may also contain conventional ingredients such as fillers, additional flame retardants (such as triperidine phosphine oxide and magnesium or aluminum hydroxide), pigments, dyes, stabilizers, anti-static agents, crystallization aids, mold release agents and the like, as well as resinous components not previously discussed.

30 Other additives that may be employed to enhance flame retardancy in the instant invention include phosphine oxides, such as triarylphosphine oxides and aromatic phosphates, especially diphosphates. Illustrative examples of triarylphosphine oxides include triphenylphosphine oxide, tritolylphosphine oxide, trinonylphosphine oxide and trinaphthylphosphine oxide. Triphenylphosphine oxide is often preferred. The aromatic diphosphates that may be employed in this invention have the formula VII

VII



40 wherein each A and A^1 are independently a substituted or unsubstituted aliphatic, alicyclic or aromatic radical and Q is a covalent bond linking a carbon in each A or a bridging radical selected from the group consisting of CH_2 , $C(CH_3)_2$, S , SO_2 , CO , O and $N=N$ and t is an integer from 0 to 4. A suitable example of an aromatic monophosphate is triphenylphosphate.

45 Additional additives that may be employed in the instant invention to enhance flame retardancy include melamine cyanurate and aluminium and magnesium hydroxide. Fillers such as mineral fillers may be added, such as calcium or barium sulphate.

55 The method for producing the blends employed in the present invention is not particularly limited, and the conventional methods are satisfactorily employed. Generally, however, melt blending methods are desirable. The time and temperature required for melt-blending are not particularly limited, and they can properly be determined according to the composition of the material. The temperature varies somewhat with the blending ratio of the polyphenylene ether to polyamide, but it is generally within a range of 270° to 350°C. A prolonged time and/or a high shear rate is desirable for

mixing, but the deterioration of the resin composition advances. Consequently, the time needs to be determined taking into account these points.

Any of the melt-blending methods may be used, if it can handle a molten viscous mass. The method may be applied in either a batchwise form or a continuous form. Specifically, extruders, Banbury mixers, rollers, kneaders and the like may be employed.

The following examples illustrate the production and properties of the flame retardant polyamide/polyphenylene ether compositions of the instant invention.

EXAMPLES

A number of blends were prepared by tumble mixing a precompounded blend of polyphenylene ether and polyamide (PA) 66, with various additives, followed by extrusion at 290°C and granulation. The granules were heated to 300°C and molded into 1.6 mm UL test bars.

The silicone oil used in the examples consists of a blend of four polymers corresponding to formula IV in the description (2 parts: w = 0; x, y, z = 5; R¹ = methyl, R² = N-2-(aminoethyl)-3-aminopropyl; R³ = methyl, 3 parts: w = 0; x, y, z = 5; R¹, R² = methyl; R³ = methyl, 2 parts: w = 0; z = 0; x = 5, y = 5; R¹, R² = methyl; R³ = H; 1 part: w = 1; x, y, z = 5; R¹, R² = methyl; R³ = methyl).

Examples 14 and 15 are based on precompounded PA-6 blends. Examples 16 and 17 were prepared from a precompounded PPE/PA blend, and separately added PA.

In the following tables the composition (in parts by weight) and the properties of the blends have been compiled.

Example Composition	1	2	3	4	5	6	7	8	9	10
PPE/PA (50/50)	100	95	98	93	89.5	89.5	89.5	89.5	89.5	89.5
Silicone oil	-	-	2	2	2	2	2	2	2	2
Zinc borate (anhydrous)	-	-	-	-	8.5	3	3	3	3	3
Boron phosphate	-	5	-	5	-	-	-	-	-	-
Aluminium metaphosphate	-	-	-	-	-	8.5	-	-	-	-
Calcium pyrophosphate	-	-	-	-	-	-	5.5	-	-	-
Trilithium phosphate	-	-	-	-	-	-	-	5.5	-	-
Magnesium metaphosphate	-	-	-	-	-	-	-	-	5.5	-
Zinc pyrophosphate	-	-	-	-	-	-	-	-	-	5.5

Vicat °C	222	221	217	218	216	218	219	217	219	219
UL-class	HB (drip)	HB (drip)	HB (drip)	V0	V1	V0	V1	V1	V1	V1
Izod/notched (kJ/m ²)	5.5	4.2	7.5	6.4	6.7	6.0	5.3	6.9	5.8	5.3

Example Composition	11	12	13	14*	15*	16	17
PPE/PA (60/40)	93	-	-	-	-	-	-
PPE/PA (50/50)	-	84.49	86.49	78	73	32	32
PA	-	-	-	-	-	51	41
Silicone oil	2	2	-	2	2	2	2
Boron phosphate	5	-	-	5	5	10	10
Aluminium metaphosphate	-	5.5	5.5	-	-	-	-
Zinc borate	-	3	3	-	-	-	-
TiO ₂	-	5	5	-	5	5	5
Carbon black	-	0.01	0.01	-	-	-	-
Calcium sulfate	-	-	-	15	15	-	10
<hr/>							
Vicat °C	213	-	-	204	205	212	230
UL-class	V1	V0	HB	V2	V1	V2	V2
Izod/notched (kJ/m ²)	4.9	4.2	4.3	3.7	3.3	2.8	2.5
CTI (V)	-	-	-	450	550	350	450

*: PA 6 based

Claims

1. Polymer composition comprising:

- a blend comprising at least one polyamide and at least one polyphenylene ether;
- at least one polymeric siloxane compound; and
- at least one boron compound.

2. Polymer composition according to claim 1, wherein the boron compound is selected from the group consisting of metal borates, boric acid, organic boron compounds, perborates, boron phosphate and mixtures of two or more of these boron compounds.
- 5 3. Polymer composition according to claim 2, wherein the boron compound is zinc borate and/or boron phosphate.
4. Polymer composition according to claim 1-3, wherein additionally at least one inorganic phosphate compound d) is present
- 10 5. Polymer composition according to claim 1-4, wherein the amount of polyphenylene ether in the polyamide-polyphenylene ether blend is not more than 95 wt %, preferably between 10 and 70 wt. %
6. Polymer composition according to claim 1-5, wherein the polymeric siloxane compound is selected from the group of polysiloxane and siloxane copolymers, such as polyphenylene ether or polyetherimide siloxane copolymers
- 15 7. Polymer composition according to claim 1-6, wherein the amount of polymeric siloxane compound is between 0.1 and 20, preferably between 1 and 5 wt % of the composition.
8. Polymer composition according to claim 1-7, wherein the amount of boron compound, calculated as atomic boron, is between 0.02 and 5 wt %, preferably between 0.2 and 1.0 wt. % of the composition.
- 20 9. Polymer composition according to claim 1-8, wherein the composition additionally contains as component e) titaniumoxide, or as component f) calcium sulphate or a combination of both
- 25 10. Polymer composition according to any one of the preceding claims, wherein the amounts of a), b), c) and optionally d), e) and f) are such that the composition meets UL-94 V2 at 1.6 mm, preferably V1 or V0.
11. Use of a combination of at least one boron compound and at least one polymeric siloxane compound for improving the flame resistance of polyamide-polyphenylene ether polymer compositions.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 11 8740

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
D, Y	EP-A-0 369 169 (GENERAL ELECTRIC) * the whole document *	1-11	C08L77/00 C08L71/12 C08K3/38
Y	EP-A-0 182 163 (GENERAL ELECTRIC) * page 1, paragraph 1 * * page 4, line 1 - page 10, line 25 * * page 14, line 4 - line 9 *	1-11	
Y	EP-A-0 543 462 (DSM) * the whole document *	1-11	
A	EP-A-0 122 699 (ICI)		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 6)
			C08L C08K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 May 1995	Examiner Leroy, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (12/82) (P04C01)

